

Description

Opalescent Glass Ceramic

5 The invention relates to an opalescent glass ceramic, in particular an opalescent glass ceramic as a dental material or as an additive to or component of dental material, comprising at least the components SiO_2 , Al_2O_3 , P_2O_5 , Na_2O , K_2O , CaO and Me(IV)O_2 .

10 Furthermore, the invention relates to a method for producing an opalescent glass ceramic as well as to the use of such a ceramic.

 Opalescent glasses are known, for example, from EP 0 622 342 B1. EP 0 622 342 B1 discloses an opalescent glass based on SiO_2 - B_2O_3 - Al_2O_3 - K_2O - Na_2O - CaO - BaO - SrO - TiO_2 - ZrO_2 - P_2O_5 - CeO_2 . The linear thermal expansion coefficients (TEC) therein
15 are either much too high (Examples 5, 15, 26, 27 with $\text{TEC} \geq 15.1$) or much too low ($\text{TEC} \leq 10.8$) to be usable for the preferred use of the material as a veneer ceramic for metal tooth restoration in pure form. To coat current alloys, a blending with further glasses is required.

20 Moreover, tests have shown that the glass ceramic products known from EP 0 622 342 B1 are too dull, so that a good aesthetic appearance is not ensured. Overall, the opalescent glass ceramic products known from EP 0 622 342 B1 exhibit a too weak and only slightly bake-stable opalescence, and a too high opacity and have
25 no fluorescence.

 A porcelain material intended for the dental field is known from US 6,022,819. It has TiO_2 or ZrO_2 as components. The SiO_2 content is preferably 50 to 85% by weight.

30 The object of the present invention is to make available an opalescent glass ceramic product, a method for producing same as well as its use, which has improved opalescence with simultaneously improved transparency and a baking temperature or thermal expansion coefficients adapted to other materials as well

as fluorescence.

According to the invention, the object is essentially achieved by an opalescent glass ceramic product of the
aforementioned type in which the opalescent glass ceramic is
devoid of ZrO_2 and TiO_2 , the glass ceramic product has a $Me(II)O$
content of less than 4% by weight and the $Me(IV)O_2$ by weight is
from 0.5 to about 3% by weight. Preferably, it is provided that
the $Me(IV)O_2$ content is composed of 0 - 1% by weight CeO_2 and 0 -
2.5% by weight SnO_2 .

In particular, the $Me(II)O$ content is 2 - 3.5% by weight,
preferably 2.5 - 3% by weight.

A preferred composition contains the following components:

Component	% by weight
SiO_2	55 - 62
Al_2O_3	13 - 17
B_2O_3	0 - 2
P_2O_5	1.5 - 3
Li_2O	0 - 2
Na_2O	7 - 12
K_2O	8 - 12
MgO	0 - 2
CaO	1 - 4
BaO	0 - 2
Tb_2O_3	0 - 3
$Me(IV)O_2$	0.5 - 3

the indicated amount of $Me(IV)O_2$ being composed of 0 - 1%

by weight of CeO_2 and 0 - 2.5% by weight SnO_2 .

In particular, the composition of the glass ceramic is distinguished by:

Component	% by weight
SiO_2	58 - 60
Al_2O_3	14 - 15
P_2O_5	2.3 - 2.6
Na_2O	9.5 - 10.5
K_2O	9 - 10
CaO	2.8 - 3.0
SnO_2	1.3 - 1.6
CeO_2	0.3 - 0.4
Tb_2O_3	0 - 2.0

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According to the invention, an improved opalescence is obtained by demixing of the glasses based on P_2O_5 and SnO_2 contents. The thermal expansion coefficient (TEC) of the ceramic according to the invention is in the range of $9.0 - 13.5 \times 10^{-6}/\text{K}$ and can be controlled by the K_2O content.

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By additionally fusing CeO_2 and/or Tb_2O_3 , it can be attained that the glass ceramic fluoresces, a desirable property for dental ceramics. A strong, neutral fluorescence is obtained by combining both oxides.

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Furthermore, the applicable baking temperature of the ceramic can be controlled by the portion of B_2O_3 , Li_2O and Na_2O and adapted to desired values. The applicable relevant baking temperature of the ceramics according to the invention are in the

range of 870 to 970°C.

On the whole, a glass ceramic is provided which satisfies all requirements with regard to aesthetic coating ceramics.

A method for producing the glass ceramic according to the invention is characterized by the following procedural steps:

- 1) weighing in the components according to one of the claims 1 to 6;
- 2) preferably mixing the mixture in a gyro mixer;
- 3) melting the mixture in a preferably gas-heated furnace such as a drip-feed crucible furnace, preferably at about 1500°C;
- 4) quenching the molten mass coming out of the furnace in a water bath and subsequent drying;
- 5) short grinding of the frit thus obtained in a mill (e.g. ball mill);
- 6) tempering the frit;
- 7) after drying, filling the frit in a mill, such as a ball mill, and grinding, preferably to about 10000 revolutions;
- 8) sifting the ground frit through a sieve, the sieve opening forming the end.

Preferably, the frit is tempered in the following manner:

- a. stacking the ground frits on quartz-coated fire-clay plates,
- b. placing the fire-clay plates in a furnace (e.g. electric furnace) heated to about 960°C,
- c. removing the plates from the furnace after about 40 minutes,
- d. quenching the fused frit cakes in a water bath.

The ground frit is preferably sifted through a sieve having a mesh size M in the range of $80 \mu\text{m} \leq M \leq 120 \mu\text{m}$, preferably $M = 100 \mu\text{m}$.

Unlike the glass ceramic known from EP 0 622 342 B1, the glass ceramic according to the invention needs no ZrO_2 and TiO_2 and the Me (II)O content remains less than 3% by weight. Moreover, by melting in CeO_2 and Tb_2O_3 , the opal ceramic of the invention exhibits fluorescence. Furthermore, the baking

temperature can be adapted to the desired application. The thermal expansion can be set by selective leucite crystallization in the ceramic according to the invention in such a way that it can be used especially for coating metal frame materials.

5 Further details, advantages and features of the invention can be found not only in the claims, the features found in them, alone and/or in combination, but also in the preferred embodiments found in the following description.

10 The invention will be described with reference to the following embodiments, wherein the Tests 1, 2, 8 to 21 are preferred and Tests 11 and 13 especially preferred. The compositions of the opal ceramic can be found in Table 1.

TABLE I (Columns 1 - 12)

Test	Ivo.15	1	2	3	4	5	6	7	8	9	10	11	12
% by weight													
SiO ₂	55.34	59.78	59.05	60.01	58.03	56.22	59.83	55.53	58.44	58.93	58.02	59.08	58.72
Al ₂ O ₃	16.09	14.52	14.63	16.45	15.91	16.83	16.4	14.71	14.23	14.44	14.34	14.48	14.78
B ₂ O ₃	0.22	0.44	0.44			1.09	1.07	2.23	0.44		1.1		
P ₂ O ₅	2.59	2.32	2.42	2.33	2.38	2.06	1.4	2.46	2.44	2.43	2.43	2.43	2.44
Li ₂ O				1.28	1.31	1.1	1.29	0.45					
Na ₂ O	9.08	9.36	9.3	4.44	6.39	5.91	6	9.97	9.84	10.03	10.01	10.04	9.13
K ₂ O	11.88	9.09	9.23	13.49	12.96	13.11	12.86	10	9.63	9.21	9.15	9.24	10.19
MgO													
CaO	2.6	2.97	2.95	0.09	1.3	1.91	0.09	2.88	2.98	2.97	2.97	2.97	2.97
BaO													
Tb ₂ O ₃													
SnO ₂		1.52	0.88	0.85	0.86	0.87		1.45	0.89	0.88	0.88	1.43	1.44
CeO ₂			1.1	1.06	0.86	0.87	1.07	0.33	1.11	1.1	1.1	0.33	0.33
ZrO ₂	1.9												
TiO ₂	0.3												
Calculated thermal expansion coefficient (Alpha x10exp.-6/K)													
		9.91		9.64			9.96	10.58	10.35				10.28
Applicable relevant baking temperature in °C													
	960	940	940	980				870	920				950
Tempering of the glass frit (Min./°C)													
		30/950	30/95		30/950								
Measured thermal expansion coefficient													
	unknown				unknown		17	unknown	12.01	unknown	unknown.		12.8
Optical values													
L*tran													
b*tran													
s. h*ref	26.5	31.6	32.8				9.4	27.4	25.6	29.3	34.9	30.3	32.9

TABLE I (Columns 13 - 22)

Test	13	13 Zr/Ti	14	15	16	17	18	19	20	21	22
% by weight											
SiO2	58.48	58.48	57.19	58.97	58.1	57.19	57.67	57.86	57.86	58.22	58.22
Al2O3	14.61	14.61	14.31	14.66	14.51	14.31	14.41	14.43	14.43	14.62	14.7
B2O3											
P2O5	2.44	2.44	2.44	2.04	2.85	2.44	2.44	2.44	2.44	2.46	2.51
Li2O											0.67
Na2O	9.9	9.9	9.85	9.91	9.88	9.85	9.86	9.87	9.87	9.19	9.21
K2O	9.93	9.93	9.79	9.8	10.03	9.79	9.82	9.86	9.86	10.94	10.1
MgO											1.43
CaO	2.86	2.86	2.67	2.86	2.86	2.67	2.67	2.67	2.67	2.83	0.07
BaO											1.3
Tb2O3			1.99			1.99	1.99	1.99	1.99		
SnO2	1.44		1.44	1.44	1.44	1.77	0.88	0.44		1.42	1.45
CeO2	0.33		0.33	0.33	0.33		0.22	0.44	0.88	0.33	0.33
ZrO2		1.22									
TiO2		0.55									
Calculated Thermal Expansion coefficient (Alpha x10exp.-6)											
	10.49	10.45	10.52	10.41	10.56	10.52	10.54	10.54	10.54	10.55	10.44
Applicable relevant baking temperature in °C											
	950	950	950	950	950	950	950	950	950	950	930
Tempering of the glass frit *(Min./°C)											
40	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/960	40/940
Measured thermal expansion coefficient											
12.6	10.59	11.5	11.24	11.08	10.53	unknown	unknown	unknown	12.34	13.23	unknown.
Optical values											
L*trans	80	78.9	80.3	83.3	78.1	82.6	79.5	80.2	75.2	76	71.3
b*trans	32.9	33.6	27.6	24.4	36.1	28.5	32.5	31	33.2	33.8	15.2
b*ref											

A comparison of the tests shows that the thermal expansion coefficient of the glass ceramic according to the invention is controllable. Thus, a thermal expansion coefficient (TEC) in the range of 9.0 to 13.5×10^{-6} can be set. In comparison to the ceramics known from EP 0 622 342 B1, which have either too low a TEC ($\leq 11 \times 10^{-6}/K$) or a too high TEC ($\geq 16 \times 10^{-6}/K$), the glass ceramic according to the invention can be set in the TEC range of 11.0 to $13.0 \times 10^{-6}/K$ for coating ceramics, which is especially important in the dental field.

Tests have shown that the SnO_2 - and/or CeO_2 - content is suitable for stimulating the crystallization of small amounts of leucite which are required for increasing the TEC.

A comparison of Test 13 with 1.44% SnO_2 with a Test in which the SnO_2 was replaced by ZrO_2 and TiO_2 according to the claims of EP 0 622 342 B1 (Test "13 Zr/Ti" in the Table), clearly shows that, in the latter Test, the TEC corresponds approximately to the mathematically determined value, assuming a homogeneous glass, which can indicate the lack of a leucite crystallization.

The examples show that the TEC in the glass ceramic of the invention can be controlled by the K_2O content when there is a sufficient Al_2O_3 content. In particular, Tests 11 to 14 and 21 show this property. Tests 15 and 16 indicate that the P_2O_5 content, which determines the extent of the phase separation of the glass, also has an effect.

By additionally fusing in CeO_2 and/or Tb_2O_3 , the glass ceramic can be caused to fluoresce. It could thereby be ascertained that fusing in only CeO_2 results in weak bluish fluorescence and Tb_2O_3 in a stronger yellow fluorescence which is not typical for natural teeth. A strong, neutral fluorescence is only obtained with a combination of both oxides, as Tests 17 to 20 show. The Tests 19 and 20 are optimal for fluorescence.

The baking temperature of the glass ceramic can be

controlled by the proportion of B_2O_3 , Li_2O and Na_2O and adapted to the desired value, as Tests 10 and 12 show. The applicable relevant baking temperatures of the glass ceramics according to the invention are in the range of 870°C to 970°C.

5 Test 13 has all of the preferred properties. The baking temperature and the TEC are ideal and, at the same time, the optical values with a transparency of L^* (Transparency) = 80 and a $\Delta b^* = 32.9$ are very good. In comparison thereto, the ceramic (Ivo. 15) prepared according to EP 0 622 342 B1 only
10 has a Δb^* of 26.5 at a transparency of L^* (transp.) = 69.7.

It should be noted that the chemical stability and bending strength of the illustrated examples meet the requirements of the relevant standards for dental ceramics (ISO 9693).

15 The exemplary embodiments according to Tests 13, 15 and 16 show the effect of the P_2O_5 content. Example 13 with a P_2O_5 content of 2.44% by weight is considered optimal, while the transparency is increased at the expense of opalescence in Example 15 with a P_2O_5 content of 2.04% by weight and an
20 increased opalescence with reduced transparency can be ascertained in Example 16 with a P_2O_5 content of 2.85% by weight.

Table 1 also shows embodiments (Tests 3, 4, 5, 6, 7 and 22) whose compositions are outside of the claimed range. In
25 this case, Tests 3 to 5 have a too high K_2O content and additionally Test 3 has too little CaO . It has been found shown that these exemplary embodiments are already too dull in the untempered state, presumably due to a too strong leucite crystallization. In spite of a too high leucite content, Test
30 6 is transparent since it only has a slight tendency to demix due to a P_2O_5 content of less than 1.5% by weight, but its opalescence is too low. In Test 7, a too high B_2O_3 content results in a strong dullness and, in Test 22, CaO was replaced by MgO and BaO which resulted in a reduced opalescence.

35 The glass ceramics according to the invention were

produced according to the following method:

1. Weighing in the raw materials as noted in Table 1.
2. Mixing the mixture in a gyro mixer.
3. Melting the mixture in a gas-heated drip-feed crucible
5 furnace at about 1500°C.
4. Quenching the molten mass running out of the furnace in
a water bath.
5. Drying the molten mass.
6. Brief grinding of the frit thus obtained in a ball mill.
- 10 7. Tempering the frit in the following manner:
 - stacking the ground frits on quartz-coated fire-
clay plates
 - placing these plates in an electric furnace heated
to 960°C
 - 15 - removing the plates from the furnace after about 40
minutes
 - quenching the fused frit cakes in the water bath.
8. After drying, filling the frit into the ball mill and
grinding, preferably to about 10,000 revolutions.
- 20 9. Sifting the ground frits through a sieve, preferably
having 100 μ m mesh size.

To measure opalescence and transparency of the opal
ceramic, it should be noted that 3 grams of the powdery opal
ceramics were compacted in a press to form a round blank and
25 these were sintered together in a dental vacuum baking furnace
at the same temperature as in Test 13 of 950°C. The round
blank thus obtained has a thickness of about 2.5 mm. In the
case of opalescence, these round blanks appear orange/yellow
with transmitted light since the unscattered long-wave light
30 catches the eye. On the other hand, when looking at it
against a dark background, the round blank appears bluish,
since the more strongly scattered short-wave light is seen in
this case.

This phenomenon can be determined quantitatively with a
35 spectrophotometer. For this purpose, the L*, a*, b* values
were measured in transmission and in reflection on a black

base in the photometer of, for example, the Minolta corporation (CM-3610d), whereby a 2° observer and standard light D65 are required. In the L*, a*, b* colour system, a positive b* value represents the yellow part of the light, on the other hand, a negative b* value represents its blue part. The higher the absolute amount, the more intense the colour.

Accordingly, the opalescent round blanks thus produce positive b* values during transmission and negative b* values during reflection. The more the two b* values deviate from one another, the stronger the opalescence.

Moreover, the L* value measured in transmission can be used as a measure for the transparency of the round blank.

Aesthetically satisfying results in dental restoration are obtained with opal ceramics whose round blanks have a Δb^* of at least 25 and L* (transm.) of at least 75.